

CATALYTIC HYDROLIQUEFACTION OF COALS FOR HYDROCARBON-TYPE ANALYSIS IN RELATION TO REFINING

by

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INTRODUCTION

Small samples of liquids have been prepared from several coals of widely varied rank by catalytic hydrogenation in a batch autoclave. The liquids were prepared at conditions designed to minimize cracking of hydrocarbon components, yet were upgraded to remove nitrogen and to permit detailed determination of hydrocarbon types potentially obtainable for refining. This paper covers the preparation and properties of the liquids; the hydrocarbon analyses will be reported later.

Scattered literature references indicate that the complexity of hydrocarbon groups in coals and in liquefaction products varies substantially with the rank or grade of coal liquefied. Reports of early German technology refer repeatedly to the liquefaction of brown coal (lignite) at about half the hydrogenation pressure required for bituminous coals (9). The asphaltene content of recycled oil in continuous hydrogenation of German coals decreased with decreasing grade of coal and reached an apparent minimum in the range of sub-bituminous coals. Although there were gaps in the data, this trend, combined with greater rates of hydrogenation observed for the product oils, indicated smaller polynuclear hydrocarbon units as well as different chemical structure in brown coals in comparison with bituminous coals. The greater reactivity was also associated with increased oxygen content. Wender (8) suggested that hydrocarbon groups in coal can vary from those which contain little more than one aromatic ring, as in lignite, to virtually one huge fused-ring aromatic in anthracite coal. However, most coal liquefaction research in this country has been done on bituminous coals. U.S. Bureau of Mines work in the 1940 era recognized the greater reactivity of lower-rank coals and the importance of catalysts in promoting formation of hydroaromatic compounds that function as hydrogen donors in liquefaction (6). In fact, low-rank coals were so reactive that high hydrogen pressure was required to avoid repolymerization of reactive fragments to coke at the temperatures used, generally about 430° C. However, almost complete liquefaction and extensive oxygen removal could be obtained at relatively low temperature and with relatively little hydrogen consumption (but with hydrogen transfer from solvent). The rate of conversion of Pittsburgh bituminous-A coal to asphaltenes was considerably greater than conversion of the asphaltenes to oil, while the opposite was true for coal of bituminous-C rank from Rock Springs, WY (9). The wt-pct yield of total oil increased with rank of coal from about 55 for lignite to 65 for sub-bituminous to 70-75 for high-volatile bituminous coal on a moisture- and ash-free (maf) basis. Yields were much less for still higher-rank medium-volatile coals because of low reactivity. These trends were observed in both batch autoclave and continuous-flow units with stannous sulfide catalyst. Characterization of the liquid products was limited to distillate fractions, usually a small part of the product, which were determined to be highly cyclic and aromatic. Phenolics content was greater in distillates from coal of lower rank.

Among more recent studies, the effluent from liquefaction of a Utah sub-bituminous coal with hydrogen donor solvent (3) contained less benzene insoluble material than that from Pittsburgh bituminous coal, and addition of a paraffinic diluent was required to precipitate enough asphaltenes for agglomeration of residual solid particles. Other sub-bituminous coal products behaved similarly. In reports of the HRI, Inc., H-Coal process (7) and the Gulf Science and Technology Co. CCL (catalytic coal liquefaction) process (4), syncrudes produced from sub-bituminous coals contained less heavy ends and less polynuclear aromatics with 4 or more rings. An extensive survey of coals

with respect to liquefaction by hydrogenation (1) confirmed early reports that high volatile bituminous coals gave the best yields, but the products were not characterized in any detail.

EXPERIMENTAL

Materials

Table 1 shows analyses of the coal samples used. The analyses were run by the U.S. Bureau of Mines, Pittsburgh, PA. The lignite was supplied by the Grand Forks, ND, Energy Research Center, the Wyodak coal by Hydrocarbon Research, Inc., Trenton, NJ, and the other four samples by Conoco Coal Development Co., Library, PA. Those samples not already pulverized were ground and screened to -50 mesh. The lignite and Wyodak coal samples were dried under vacuum and kept under nitrogen thereafter. The others were used as received. Note that the nitrogen content of the bituminous coals was about 50 percent greater than that of the sub-bituminous coals and lignite. Indicated oxygen content of the dry coals increased from about 8 to 19 wt pct as the rank or grade decreased. The W. Kentucky coal had a high sulfur content of 4.3 wt pct.

TABLE 1. - Analyses of Coals

Source	PA-WV	Illinois	W. KY	Montana	Wyoming	N. Dakota
Seam	Pittsburgh	No. 6	--	(Colstrip)	(Wyodak)	Beulah Std. II
Rank	hvb A	hvb B or C	hvb B or C	sub-bit. A	sub-bit. C	Lignite
Proximate analysis (as received)						
Moisture	1.7	7.8	2.9	4.2	10.9	28.0
Volatile matter	35.9	34.2	38.4	34.4	39.5	31.0
Fixed carbon	55.1	51.4	48.8	48.5	42.7	33.3
Ash	7.3	6.6	9.9	12.9	6.9	7.7
Ultimate analysis (moisture free)						
Hydrogen	5.1	4.9	4.9	4.3	4.8	4.5
Carbon	76.9	75.2	70.2	65.2	66.8	63.5
Nitrogen	1.5	1.6	1.4	0.6	1.0	0.9
Sulfur	1.6	1.5	4.3	1.8	0.5	1.3
Oxygen (difference)	7.6	9.7	8.8	14.5	19.2	19.1
Ash	7.4	7.1	10.2	13.5	7.8	10.7

Nickel-molybdenum/alumina hydrotreating catalyst, American Cyanamid HDS-3A, was crushed, screened to 60-100 mesh, and dried overnight at 200° C. Elemental sulfur was added in liquefaction runs to provide some sulfiding of the catalyst. For upgrading the crude liquids, the catalyst was presulfided in the autoclave as a slurry in n-octane plus carbon disulfide, 400 psig added hydrogen, and at 285° C maximum temperature. The diluent was flashed off at 225° C to insure elimination of water.

The initial solvent for each preparation was 99 percent tetralin from the Aldrich Chemical Co.

Procedure

Both liquefaction and upgrading runs were made in a 2-liter Magne-drive autoclave from Autoclave Engineers, Inc. A typical liquefaction charge was 325 - 400 g coal, 500 g solvent, 50 g catalyst, and 4 g sulfur. The charged reactor was purged with nitrogen and hydrogen, pressured with hydrogen to about 1,500 psig, leak tested, and heated to 300° C in about one hour. The temperature was then raised slowly over a period of several hours, depending upon the rate and extent of hydrogen consumption, to a maximum of 400° C. Cylinder hydrogen was boosted to about 3,300 psig with a Whitey compressor, and it was added periodically to the reactor from a calibrated surge volume to maintain reactor pressure between about 2,450 and 2,700 psig. At the end of a run the reactor was cooled rapidly to 260° C, and nearly all the gaseous components were bled off to remove water and some light ends. The effluent gas passed through a condenser and ice-cooled trap, a scrubber column filled with 1/4-inch screen saddle-type packing, and a second ice-cooled trap, after which it was sampled and metered. The top section of the packed column was heated to break the fog which passed the first trap. The product slurry, cooled to about 70° C, was removed from the reactor by suction through a dip tube and was filtered through Whatman No. 41 paper in a heated Buchner funnel, at 50 - 60° C. Filtered liquid product was used as diluent for the following run. The filter cake was washed with benzene at 50° C and dried to determine residual solids. Runs were repeated until the calculated tetralin content of the recycled liquid was less than 6 wt pct, and then were continued to accumulate at least 1,200 g of crude liquid (including benzene washings and light ends). The reactor was flushed with hot benzene only at the end of a series, since complete recovery from single runs was not essential. The reactor was opened occasionally to inspect for accumulated deposits, which generally were insignificant.

The crude liquids were upgraded in similar autoclave runs to remove heteroatoms, especially nitrogen. A typical charge was 100 g presulfided catalyst and 850 g crude liquid.

Effluent gases were analyzed by gas chromatography. Hydrogen consumption was taken as the difference between that charged and withdrawn. No attempt was made to account for sulfur, nitrogen, or oxygen, although water recovery was nearly quantitative in later runs. Overall material balances were calculated, recognizing the limitations of the procedures used, but the objective was to obtain liquids which contained most of the hydrocarbons potentially obtainable from the coal, not to provide quantitative process data.

The upgraded liquids were vacuum distilled in a Perkin-Elmer spinning band column to an overhead temperature of 425° C, corrected to atmospheric pressure. Asphaltenes were removed from the > 425° C residuum by pentane precipitation (5), and the asphaltene-free residuum was then vacuum flashed at 540° C, corrected to atmospheric pressure.

RESULTS

The results of the liquefaction experiments are summarized in Table 2. The data for each coal are a composite of those for successive batches from which product liquid was retained. Total products accounted for varied from 90 to 105 wt pct of coal charged. The variations reflected mostly uncertainty in reactor holdup at the start of product accumulation, incomplete recovery of water and possibly removal of sulfur from W. Kentucky coal. Net yields of liquid varied from 69 wt pct from Illinois coal to 55 wt pct from lignite. The yields of C₁ - C₄ light gases decreased and that of CO₂ increased as the rank of coal decreased. Hydrogen consumption increased by about 15 percent as the rank of coal decreased, with the exception of Pittsburgh coal to be noted later. The reaction times briefly summarized in Table 2 show that the major part of the reaction was at temperatures less than 375° C, except for Pittsburgh coal, and that less total time was required to yield a readily filterable product slurry from the lower-rank coals.

TABLE 2. - Batch Liquefaction of Coals
2,450-2,800 psig, NiMo Catalyst

Coal	Pittsburgh	Ill. No. 6	W. Ky.	Colstrip	Wyodak	Lignite
Wt-pct of coal charge:						
Net liquid	66	69	62	58	60	55
Gas: C ₁ - C ₄	5.8	5.0	5.2	3.2	4.2	4.2
C ₅ +	2.8	0.9	1.0	1.3	2.2	2.2
CO ₂	0.1	0.5	0.7	3.2	5.6	5.6
Residual solids	19	19	18	32	21	20
Total products	101	97	90	104	106	102
H ₂ consumed	4.3	4.0	4.0	4.4	4.8	4.6
Reaction time, hrs. at °C:						
325 - 375	5.2	7.6	10.3	6.8	6.8	5.6
376 - 400	5.2	2.6	2.0	2.1	1.9	1.6
Total	10.4	10.2	12.3	8.9	8.7	7.2

Most of the hydrogen consumption also occurred at less than 375° C, again with the exception of Pittsburgh coal.

Averaged temperature-time curves for the liquefaction reactions are shown in Figure 1. Temperatures were increased as needed to maintain a suitable rate of hydrogen consumption. The maximum temperature was set at 400° C to minimize hydrocarbon cracking, except for an initial preparation from Illinois coal for which data are not included. Temperatures up to 415° C were used in that series, and yields of methane increased significantly. The bituminous coals showed no substantial consumption of hydrogen, as indicated by pressure decrease, at less than about 350° C. Pittsburgh coal was the least reactive, with the indicated rate of hydrogen consumption being about half that of the other bituminous coals and one-third that of the lower-rank coals. To overcome this, maximum reactor pressure for Pittsburgh coal was increased to 2,800 psig. Coupled with less production of water, this resulted in sharply increased partial pressure of hydrogen in the reactor. Reaction rates actually increased as the series progressed, in contrast to behavior of the other coals. This improved rate was attributed to the formation of hydroaromatics of higher molecular weight which were better hydrogen donor solvents than the tetralin used as starting solvent. Hydrogen consumption by the sub-bituminous coals and lignite began at 325° C or less, as reflected in the curves of Figure 1, and most of the hydrogen was consumed at less than 350° C. In fact, too rapid an increase in reaction temperature for these coals resulted in an overall decrease in hydrogen consumption and a viscous product which was difficult to handle. Reaction temperature was still programmed to 400° C, however, for increased heteroatom removal from the liquid and resultant molecular weight decrease.

The results of upgrading the crude coal liquids by similar batch hydrogenations with pre-sulfided catalyst are summarized in Table 3. Results for the Wyodak coal were not complete when the manuscript was submitted. The objective was to decrease nitrogen content of the liquids to 0.2 to 0.3 wt pct with a minimum of cracking of hydrocarbons. The ratio of oil to catalyst in the autoclave was far greater than in a typical trickle-flow operation over fixed-bed catalyst, by a factor of up to 50-fold. Thus, longer reaction time was required, and

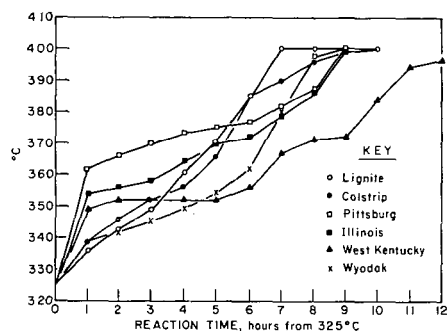


FIGURE 1 LIQUEFACTION OF COALS

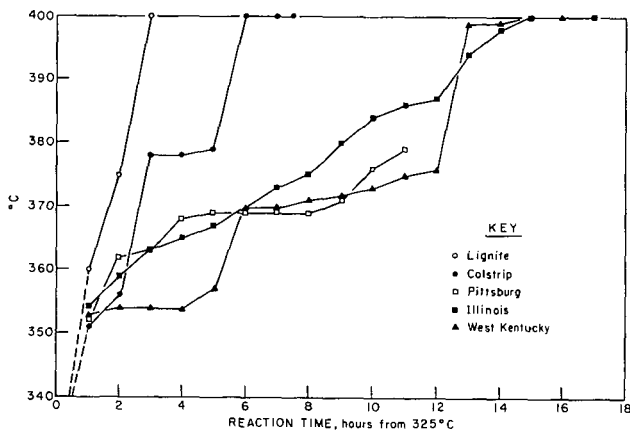


FIGURE 2 UPGRADEING OF COAL LIQUIDS

TABLE 3. - Upgrading Coal Liquids
2,450 - 2,650 psig, NiMo Catalyst (Presulfided)

Coal	Pittsburgh	Ill. No. 6	W. Ky.	Colstrip	Lignite
Wt-pct of charge:					
Liquid product	92	92	92	93	95
Gas: C ₁ - C ₄	0.3	1.8	2.0	0.8	0.3
C ₅ +	1.0	0.8	0.8	0.2	0.9
Total products	95	97	97	97	98
H ₂ consumed	1.0	2.3	2.3	1.6	0.9
Reaction time, hrs. at °C:					
325 - 375	9.8	8.7	12.7	4.7	2.0
376 - 400	<u>0.9</u>	<u>9.3</u>	<u>6.4</u>	<u>2.9</u>	<u>0.7</u>
Total	10.7	18.0	19.1	7.6	2.7

increased temperature could not be substituted for time without increased cracking of hydrocarbons originally present. The liquids from Illinois and W. Kentucky coals required up to 19 hours reaction time; however, even in those runs over 60 percent of the hydrogen was consumed at less than 375° C. Much shorter reaction times were required for upgrading the liquids from lower-rank coals and lignite. Recovery of upgraded liquid was 92 to 95 wt pct of the charge, not including C₅ + material in the effluent gas. Hydrogen consumptions and yields of gaseous hydrocarbons were small, except for the two liquids which required extended reaction. Temperature-time curves for the upgrading are shown in Figure 2. No appreciable hydrogenation occurred at less than 350° C, and reactions of all except the Pittsburgh liquid were programmed to 400° C. The Pittsburgh run was cut short when that liquid was found to have been substantially upgraded during the liquefaction as previously noted.

Properties and some elemental analyses of the crude and upgraded liquids are given in Table 4. Nitrogen content of the crude liquids from bituminous coals was 1.1 to 1.3 wt pct, compared to 0.4 to 0.6 wt pct in those from lower-rank coals. The exception, again, was that from Pittsburgh coal, for which more hydrogenation during liquefaction had decreased nitrogen content to 0.4 wt pct. Oxygen content in several of the crude liquids, determined by neutron activation analysis, was 1.3 to 2.1 wt pct. Nitrogen content of all the upgraded liquids was decreased to about the same level, in the range of 0.2 to 0.3 wt pct. Sulfur content was, of course, small in all cases. The upgraded liquid from Pittsburgh coal was the most viscous, but differences were small since the extent of upgrading was controlled to bring all liquids to the same nitrogen content. Pour points of the upgraded liquids varied from less than 5° F for liquids from bituminous coals to +45° F for that from lignite, reflecting increased paraffin content in the latter. However, a few percent of waxy n-paraffins can increase pour point sharply.

Distributions of the upgraded liquids by distillation and asphaltene content are shown in Table 5. Asphaltene contents were in the range of 4.7 to 6.8 wt pct and, thus, correlated well with nitrogen contents to indicate that all liquids had been brought to a similar level of upgrading to a predominantly hydrocarbon product. The distribution by boiling range was similar for all the liquids. This may be surprising in view of the greater reactivity of the lower-rank coals, but relatively little upgrading of the crude liquid was required in those cases.

TABLE 4. - Properties of Crude and Upgraded Coal Liquids

Coal	Pittsburgh	Ill. No. 6	W. Ky.	Colstrip	Lignite
Crude liquid:					
Nitrogen, wt-pct	0.44	1.10	1.28	0.64	0.43
Oxygen, wt-pct	-	1.34	2.09	1.61	-
Upgraded liquid:					
Specific gravity, 60/60° F	0.99	0.99	0.99	0.99	0.98
SSU vis. @ 100° F	441	126	89	263	181
Pour point, ° F	+5	<5	<5	+20	+45
Carbon, wt-pct	89.2	88.6	88.2	88.1	89.0
Hydrogen, wt-pct	10.8	10.3	10.7	10.6	10.8
Sulfur, wt-pct	<.01	.02	.02	<.01	<.01
Nitrogen, wt-pct	.20	.25	.29	.19	.25
Oxygen, wt-pct	-	.19	.32	.32	-

TABLE 5. - Distribution of Upgraded Coal Liquids

Coal	Pittsburgh	Ill. No. 6	W. Ky.	Colstrip	Lignite
Distillation, wt-pct					
<200° C	10.0	11.4	16.6	11.5	12.3
200 - 325° C	21.7	27.9	26.1	21.5	24.0
325 - 425° C	20.3	22.5	22.8	21.1	20.7
425 - 540° C*	26.6	23.7	19.7	21.0	21.0
>540° C*	16.2	7.5	9.3	18.3	15.0
Asphaltenes	4.7	6.8	5.2	6.6	6.7

*Asphaltenes removed from > 425° C resid.

Table 6 gives the specific gravities and nitrogen contents of the distillation fractions. The trends are as expected, with nitrogen concentration greatest in the residuum.

DISCUSSION

The results reported here indicate that a wide variety of coals can be liquefied by catalytic hydrogenation at conditions which permit recovery of most of the hydrocarbons potentially obtainable from a given coal. By control of the extent of upgrading of the crude product, liquids of which about 90 percent can be analyzed for hydrocarbon type have been prepared. Such analyses will provide information on the effect of coal source on the character of potential feedstocks for production of refined fuels. Differences in the required extent of upgrading of the crude liquids may have decreased the spread in complexity of hydrocarbon types recovered, but in view of the relatively low reaction temperatures used and the small yields of gaseous hydrocarbons, not much

TABLE 6. - Distillation Fractions of Upgraded Liquids

Coal	Pittsburgh	Ill. No. 6	W. Ky.	Colstrip	Lignite
<200° C distillate:					
Specific gravity	0.829	0.827	0.832	0.822	0.822
Nitrogen, wt-pct	.003	.001	.096	.023	.007
200 - 325° C distillate:					
Specific gravity	.915	.926	.919	.918	.916
Nitrogen, wt-pct	.016	.021	.062	.030	.104
325 - 425° C distillate:					
Specific gravity	.983	1.001	.993	.982	.983
Nitrogen, wt-pct	.076	.159	.200	.119	.304
425 - 540° C distillate:*					
Specific gravity	1.045	1.061	1.049	1.032	1.032
Nitrogen, wt-pct	.272	0.415	0.415	0.233	0.412
>425° C resid.					
Sulfur, wt-pct	<.01	<.01	.04	.02	<.01
Nitrogen, wt-pct	.37	.56	.57	.33	.50
Asphaltenes, wt-pct	9.9	17.9	15.3	14.3	15.7

*Asphaltenes removed

cracking of heavier hydrocarbons should have occurred. The reaction conditions used for lignite, for example, could not have been applied to Illinois coal to recover any substantial part of the hydrocarbons for analysis. On the other hand, a crude liquid from one of the low-rank coals could be upgraded on the same temperature-time program as was used for Illinois coal, and this is planned.

The upgraded coal liquids described in this paper are being analyzed in detail for hydrocarbon-type composition by methods developed for petroleum and adapted to the analysis of synthetic crude oils (2). The results will be reported later when completed.

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